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(71) Applicant (for all designated States except US): F.L. SMIDTH & CO. A/S [DK/DK]; Vigerslev Allé 77, DK-2500 Valby (DK).

(72) Inventor; and

(75) Inventor/Applicant (for US only): THOMSEN, Kent [DK/DK]; Vigerslev Allé 77, DK-2500 Valby (DK).

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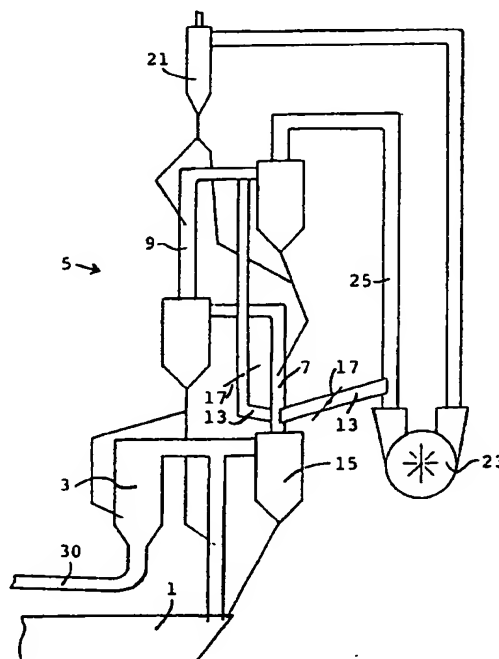
With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD FOR REDUCING THE SULPHUR DIOXIDE CONTENT IN THE FLUE GAS FROM A CLINKER PRODUCTION PLANT AND APPARATUS FOR CARRYING OUT THE METHOD

(57) Abstract

The invention provides for a method for the reduction of the SO₂ content in the flue gas from the kiln system of a clinker production plant, comprising a cyclone preheater (5) with a number of cyclone stages, a bottom and separation cyclone (15) and a precalciner (3). By this method the finest raw meal particles having a large specific surface area and a high content of free CaO and being entrained in the flue gas, are extracted from the flue gas outlet duct (7) of the separation or bottom cyclone (15) of the preheater, are directed past at least one cyclone stage and are re-introduced into the flue gas somewhere downstream of the said cyclone stages. Hereby it is obtained that the free CaO reacts with SO₂ to form CaSO₃, which, after further reaction in the precalciner (3), ends up in the rotary kiln as CaSO₄ or in a filter after the preheater (5) as CaSO₃.



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Method for reducing the sulphur dioxide content in the flue gas from a clinker production plant and apparatus for carrying out the method.

5 The present invention relates to a method for reducing the sulphur dioxide content in the flue gas from a clinker production plant which comprises a cyclone preheater with a number of cyclone stages, a bottom and separation cyclone and a precalciner. Furthermore, the invention relates to an
10 apparatus for carrying out the method.

The kiln system of a typical clinker production plant for burning cement raw meal comprises primarily a rotary kiln and a cyclone preheater. The cement raw meal is fed to the
15 kiln system at the upper stage of the cyclone preheater, whereas the fuel for the burning is supplied to the system at the material outlet end of the rotary kiln. To-day the majority of such plants further comprise a calciner stage in the lower section of the cyclone preheater, to which
20 calciner fuel is also supplied. During operation of the kiln system there will be a flow of material in the direction from the upper stage of the cyclone preheater towards the outlet end of the rotary kiln, and a flow of flue gas in the opposite direction. Thus, the temperature
25 will be highest in the burning zone of the rotary kiln and decreasing in the flue gas flow direction towards the upper stage of the cyclone preheater.

Sulphides, disulphides and organically bound sulphur
30 supplied to the kiln system in the raw materials are already capable of forming SO_2 in the upper stage of the cyclone preheater when the temperature of the materials exceeds about 300°C . In those cases where a so-called semi-dry kiln system is used the raw materials being
35 supplied in hydrous suspension together with hot flue gas to a drier crusher before the raw meal produced herein is supplied to the kiln system per se, the formation of SO_2 can take place in the drier crusher, where the temperature typically drops from about 750°C to about 150°C , depending
40 on the water percentage in the supplied material.

A part of the formed SO_2 reacts immediately on to CaSO_3 , e.g. by reaction with CaO or CaCO_3 . The formed CaSO_3 is either collected in the filter for the flue gas cleaning or reacts on in the calciner to CaSO_4 , whereafter it ends up in the clinker material.

Further, a part of the SO_2 may be collected in a conditioning tower, if any, for cooling the flue gas and/or in a raw mill, if any, for producing raw meal, and using flue gas for drying. The remaining SO_2 will be emitted into the atmosphere.

By a known method for reducing the SO_2 emission an absorbent is introduced into the gas flow immediately before the top or second from the top cyclones stages of the preheater. The absorbent is often either Ca(OH)_2 or CaO , forming CaSO_3 and possibly H_2O by the reaction with SO_2 .

By this method the formed CaSO_3 , as mentioned above, ends up either in the rotary kiln as CaSO_4 together with the rest of the raw meal or in the filter after the preheater. The disadvantage of this method is, however, that it requires a large quantity of absorbent relative to the desired degree of cleaning and that it therefore is connected with high operating costs. Moreover, it is necessary to install an absorbent feeding and controlling system which is expensive and requires quite some maintenance.

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From DE-OS 38 17 356 and US-PS 4.634.583 methods are known, by which calcined raw meal is extracted from the material outlet of the bottom cyclone of the cyclone preheater to serve as absorbent. By the method described in the DE-publication, the extracted calcined raw meal is, after cooling and slaking, introduced into the gas flow at one or

several positions higher up in the cyclone preheater, whereas by the method described in the US patent, it is directed to a mixing chamber which is situated after the preheater seen in the flue gas flow direction, and where
5 the calcined raw meal is mixed with the flue gas before the latter is directed to, e.g., a filter.

The disadvantage of using calcined raw meal extracted from the material outlet of the bottom cyclone, is that, it is
10 the coarsest fraction of the material which in this manner is extracted and since the efficiency of the flue gas desulphurization increases with increasing degree of fineness of the absorbent, it is evident that the optimum efficiency cannot be obtained.

15 By another known method dust from the main filter is used to reduce the SO_2 content in the flue gas. But since the dust from the main filter usually has a low content of CaO , it is not suitable as SO_2 absorbent in this connection.

20 The object of the present invention is to provide a method and an apparatus for reducing the sulphur dioxide content in the flue gas from a clinker production plant, which method provides for a more optimal desulphurization than
25 the known methods and which apparatus is cheaper to install and to operate.

This is according to the present invention obtained by a method of the kind mentioned in the introduction and
30 characterized in that a part of the flue gas with its content of suspended and calcined raw meal/dust is extracted from the flue gas outlet duct of the bottom cyclone, that the extracted part is by-passed via a duct past at least one cyclone stage and re-introduced in
35 the main part of the flue gas somewhere downstream of the said cyclone stages as seen in the flow direction of the

flue gas.

By this method the finest fraction of the calcined raw meal leaving the bottom cyclone is extracted which fraction is the one being entrained by the flue gas up through the cyclone preheater. As the calcined raw meal used as absorbent according to the present invention thus is much finer than according to hitherto known methods using absorbents extracted from the kiln system, a much higher desulphurization efficiency is obtained, due to the larger specific surface of the absorbent.

As mentioned, the calcined raw meal/dust will form CaSO_3 when brought into contact with SO_2 produced in the upper stages of the cyclone preheater or in a drier crusher mounted before the preheater. CaSO_3 is more thermally stable than various sulphides and organically bound sulphur, and depending on the fineness, it will therefore either end up in the main filter or continue to the precalciner, from where it after additional reaction will end up in the rotary kiln as CaSO_4 . The content of sulphur dioxide in the flue gas leaving the plant is thus reduced considerably without any substantial increase of the operating costs.

Since it is important for the SO_2 reduction that the extracted part of the flue gas is re-introduced into the main part in or immediately after the zone of the process where SO_2 is formed, it is re-introduced in the inlet duct and/or the flue gas outlet duct of the second cyclone and, if a drier crusher is used, also in the duct for supply of flue gas and raw material slurry to said crusher. Hereby it is obtained that the extracted calcined raw meal is re-introduced at such process stages where its utilization is most favourable.

Due to the flue gas rotation in the flue gas outlet duct of the bottom cyclone the dust concentration will be higher close to the wall of the outlet duct than in the middle of the latter and therefore the part of the flue gas is advantageously extracted tangentially through a tangentially extending helical extraction duct mounted on the flue gas outlet duct of the bottom cyclone. Hereby it is obtained that the dust concentration in the extracted flue gas is higher than the average dust concentration in the flue gas from the bottom cyclone.

By passing an amount of flue gas, having a relatively high temperature, from the bottom cyclone directly to one of the upper preheater stages or to the drier crusher, the heat losses from the kiln system will increase to an undesired level, and since the amount of SO_2 which is formed can vary a lot it will be advantageous to be able to regulate the amount of flue gas which is directed through the by-pass duct. Therefore, the amount of flue gas which is extracted may advantageously be regulated as a function of the SO_2 content in the flue gas from the plant and in such a manner that the extracted amount of flue gas represents 0-30%, preferably 5-15% and most preferentially 10% of the total flue gas amount in the flue gas outlet duct of the bottom cyclone. Therefore, the apparatus according to the invention preferably comprises means for regulation of the flue gas amount to be extracted, which means may comprise adjustable dampers.

The temperature of the extracted flue gas may be regulated so that the temperature of the entrained absorbent when reintroduced in the flue gas flow is in the range from 0-200°C or in the range from 600-900°C, within which temperature intervals the maximum absorption ability of the absorbent is lying.

The apparatus according to the invention may furthermore comprise means mounted in the by-pass duct for introducing cooling water into the flue gas, which is advantageous or even necessary in certain cases.

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The invention will now be described in further details with reference to the drawing being diagrammatical, and showing in

10 Fig. 1 a kiln system comprising a rotary kiln, a precalciner and a four-stage cyclone preheater, and provided with a by-pass duct according to the invention,

15 Fig. 2 a semi-dry type kiln system comprising a rotary kiln, a precalciner, a two-stage cyclone preheater and a drier crusher, and provided with a by-pass duct according to the invention,

20 Fig. 3 a semi-dry type kiln system comprising a rotary kiln, a precalciner, a three-stage cyclone preheater and a drier crusher, and provided with two by-pass ducts according to the invention,

25 Fig. 4 an extraction duct according to the invention, mounted on the flue gas outlet duct of the bottom cyclone of the cyclone preheater, and

30 Fig. 5 a curve for the utilization percent of CaO in relation to the temperature.

The kiln system shown in Fig. 1, which is used for burning e.g. cement raw meal, comprises a rotary kiln 1, a precalciner 3, a cyclone preheater 5 with four cyclones of which one is a bottom and separation cyclone 15. Raw meal is introduced at 6 into a flue gas duct 9, connecting the

two upper cyclones of the preheater, and is preheated by passing through the three cyclones in counterflow of flue gas, after which the meal is calcined in the precalciner 3 and separated from the flue gas by the separation cyclone 15 from the bottom outlet of which the raw meal is supplied to the rotary kiln 1.

The flue gas from the rotary kiln 1 and the precalciner 3 is passed from the precalciner 3 through the separation cyclone 15 and further up through the preheater 5.

From the separation cyclone 15 the flue gas will draw the finest raw meal particles up through the flue gas duct 7, in which the suspension of flue gas and raw meal particles is mixed with raw meal from the above-lying cyclone.

According to the invention a part of the flue gas/raw meal suspension is extracted through a by-pass duct 13 before a mixture takes place with the raw meal arriving from above, and whilst the suspension is still whirled in a helical path provided by the bottom cyclone 15. From the by-pass duct 13 the suspension is reintroduced into the main part of the flue gas through an opening in a flue gas outlet duct 9 and/or a flue gas inlet duct 11 of a preheater cyclone.

Fig. 2 shows a semi-dry type kiln system which comprises a rotary kiln 1, a precalciner 3 and a cyclone preheater 5 with two cyclones. The system also comprises a drier crusher 23 for drying and crushing the raw materials which are supplied as a slurry via a duct 25. The dried and crushed raw materials are introduced into the cyclone preheater from a separation cyclone 21. Air from a clinker cooler is supplied to the precalciner 3 via a duct 30.

In this system the flue gas is also drawn from the rotary

kiln 1 and the precalciner 3 up through the preheater 5 and from there to the inlet duct 25 of the drier crusher 23, in which duct 25 the gas is mixed with the raw material slurry.

5

In this system the formation of SO_2 can take place in the upper cyclone as well as in the drier crusher. SO_2 in the upper cyclone will, however, immediately react into CaSO_3 as a consequence of the CaO content in the flue gas deriving from the flue gas outlet duct 7 of the bottom cyclone 15. According to the invention, a part of the flue gas/raw meal suspension is furthermore extracted from the flue gas outlet duct 7 of the bottom cyclone 15 and directed via a by-pass duct 13 to the duct 25 for supply of material and flue gas to the drier crusher 23.

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The kiln system shown in Fig. 3 substantially corresponds to that in Fig. 2, with the exception that the cyclone preheater 5 comprises 3 cyclones.

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In this system a part of the flue gas/raw meal suspension is also extracted from the outlet duct 7 of the bottom cyclone 15. In this embodiment of the invention the suspension may, via by-pass ducts 13, be directed to the flue gas outlet duct 9 of the second cyclone or to the inlet duct 25 of the drier crusher 23.

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The embodiments shown in Figs. 1-3 of the apparatus according to the invention serve as examples only and are in no way to be considered as limiting for the scope of protection of the invention, as other embodiments are conceivable, e.g. those using preheaters with more than three cyclones.

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For regulating the flue gas amount through the by-pass ducts 13, these are provided with controlling means 17

35

which advantageously may be adjustable dampers.

The flue gas discharged through the flue gas outlet duct 7 of the bottom cyclone 15 moves in the duct along a helical path provided by the bottom cyclone 15, and Fig. 4 shows an advantageous embodiment of an extraction duct 13a mounted on the flue gas outlet duct 7.

Fig. 5 shows a curve of the utilization percent of CaO in relation to the temperature. The curve shows clearly that the reactivity of CaO varies much as function of the temperature and is, in the case shown, smallest in the temperature interval from approx. 200-600°C, and it should therefore be sought to introduced the flue gas CaO in zones of temperatures outside this interval. The curve is, of course, not general, because other factors such as water content and SO₂ content, also influence the utilization percent. Therefore, a curve must be plotted for each individual plant to find the temperature intervals within which an optimum utilization is obtained.

When the calcined raw meal extracted with the flue gas through the duct 13 comes into contact with SO₂ in the upper stages of the preheater 5 or in the drier crusher 23, CaSO₃ will be formed and the total emission of SO₂ into the atmosphere is reduced.

PATENT CLAIMS

1. A method for reducing the sulphur dioxide content in the flue gas from a clinker production plant which comprises a cyclone preheater (5) with a number of cyclone stages, a bottom and separation cyclone (15) and a precalciner (3), characterized in, that a part of the flue gas with its content of calcined raw meal/dust is extracted from the flue gas outlet duct (7) of the bottom cyclone (15), that the extracted part is by-passed via a duct (13) past at least one cyclone stage and re-introduced in the main part of the flue gas somewhere downstream of the said cyclone stage(s) as seen in the flow direction of the flue gas.
2. A method according to claim 1, characterized in, that the extracted part of the flue gas is re-introduced into the main part of the flue gas in the zone of the process where SO_2 is formed from sulphides, disulphides and organically bound sulphur.
3. A method according to claims 1 and 2, characterized in, that the extracted part of the flue gas is re-introduced in the main part of the flue gas in the inlet duct (11) and/or the flue gas outlet duct (9) of the second cyclone.
4. A method according to claims 1 and 2, characterized in, that the extracted part of the flue gas is re-introduced in a duct (25) for supply of flue gas and raw material slurry to a drier crusher (23).
5. A method according to claims 1-4, characterized in, that the extracted part of the flue gas is extracted tangentially from the flue gas outlet duct (7) of the bottom cyclone (15).

6. A method according to claims 1-4, c h a r a c t e -
r i z e d i n, that the extracted part of the flue gas
is regulated so that it represents 0-30%, preferably 5-15%
and most preferentially 10% of the total flue gas amount
5 passing the flue gas outlet duct (7) of the bottom cyclone.
7. A method according to claims 1-4, c h a r a c t e -
r i z e d i n, that the amount of flue gas, which is
extracted, is regulated as a function of the SO₂ content in
10 the flue gas from the plant.
8. A method according to claim 1, c h a r a c t e -
r i z e d i n, that the temperature of the extracted flue
gas is regulated so that the temperature of the entrained
15 absorbent, when re-introduced in the flue gas flow, is in
the range from 0-200°C or in the range from 600-900°C.
9. A method according to claim 1, c h a r a c t e -
r i z e d i n, that cooling water is injected into the
20 by-pass duct (13).
10. An apparatus for carrying out the method according to
any of the previous claims and which comprises a kiln
system with a cyclone preheater (5) with a number of
25 cyclone stages, a bottom and separation cyclone (15) and a
precalciner (3), c h a r a c t e r i z e d i n, that it
further comprises a by-pass duct (13) which extends from
the flue gas outlet duct (7) of the bottom cyclone (15) to
somewhere downstream of the succeeding cyclone in the flow
30 direction of flue gas.
11. An apparatus according to claim 10, c h a r a c t e -
r i z e d i n, that the by-pass duct (13) extends from
the flue gas outlet duct (7) of the bottom cyclone (15) to
35 the inlet duct (11) and/or the flue gas outlet duct (9) of
the second cyclone.

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12. An apparatus according to claim 10, characterized in, that the by-pass duct (13) extends from the flue gas outlet duct (7) of bottom cyclone (15) to the duct (25) for supply of flue gas and raw material slurry to the
5 drier crusher (23).

13. An apparatus according to claims 10-12, characterized in, that it comprises means (17) for regulation of the amount of flue gas to be extracted.

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14. An apparatus according to claim 13, characterized in, that the means (17) comprise adjustable dampers.

15 15. An apparatus according to claims 10-12, characterized in, that the opening for extraction of flue gas from the flue gas outlet duct of the bottom cyclone (15) comprises a tangentially extending helical extraction duct (13a).

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16. An apparatus according to claims 10-12, characterized in, that means for introduction of cooling water in the flue gas are provided in the by-pass duct (13).

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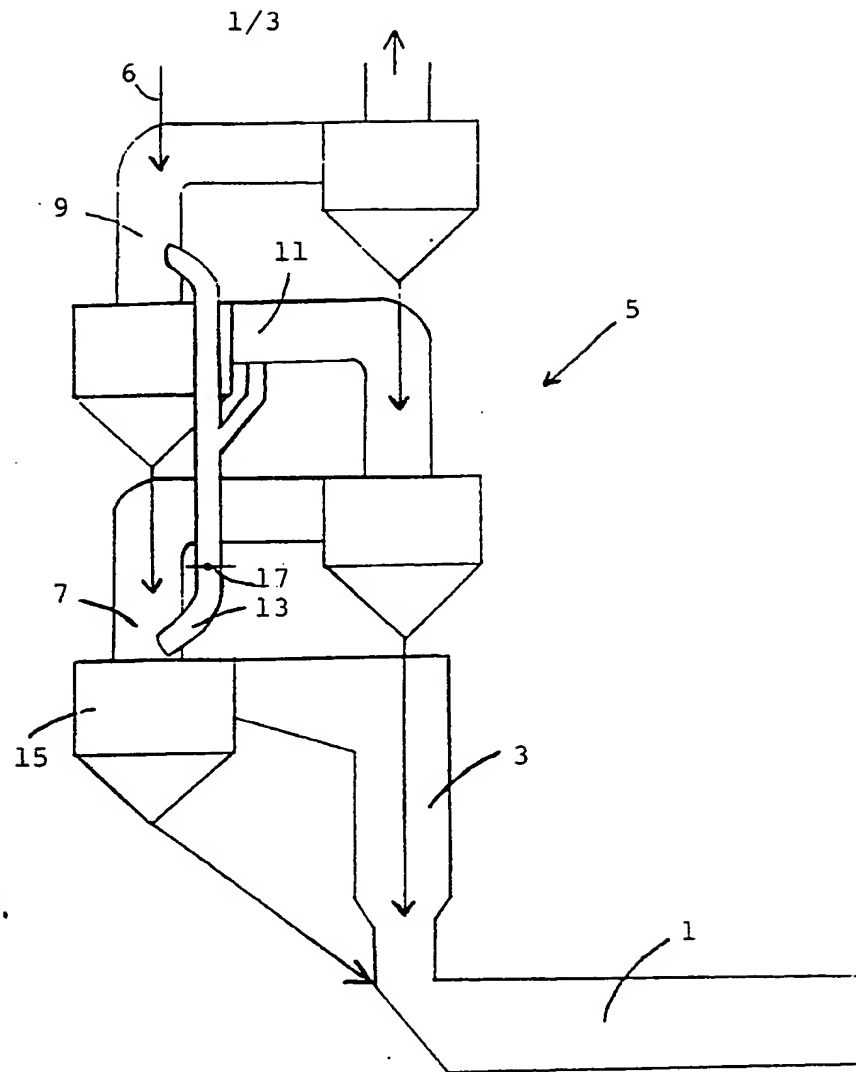


Fig. 1.

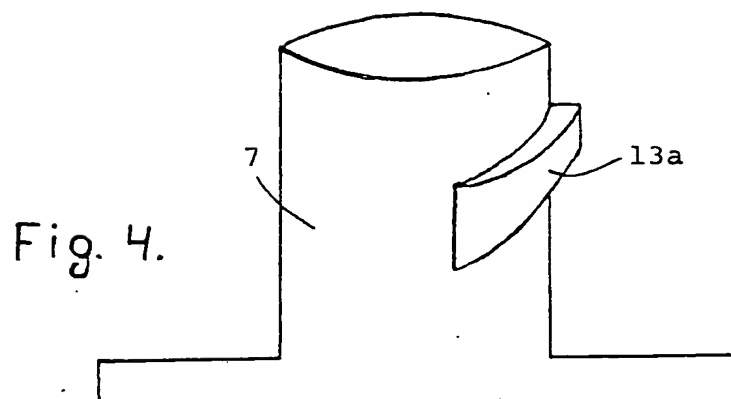


Fig. 4.

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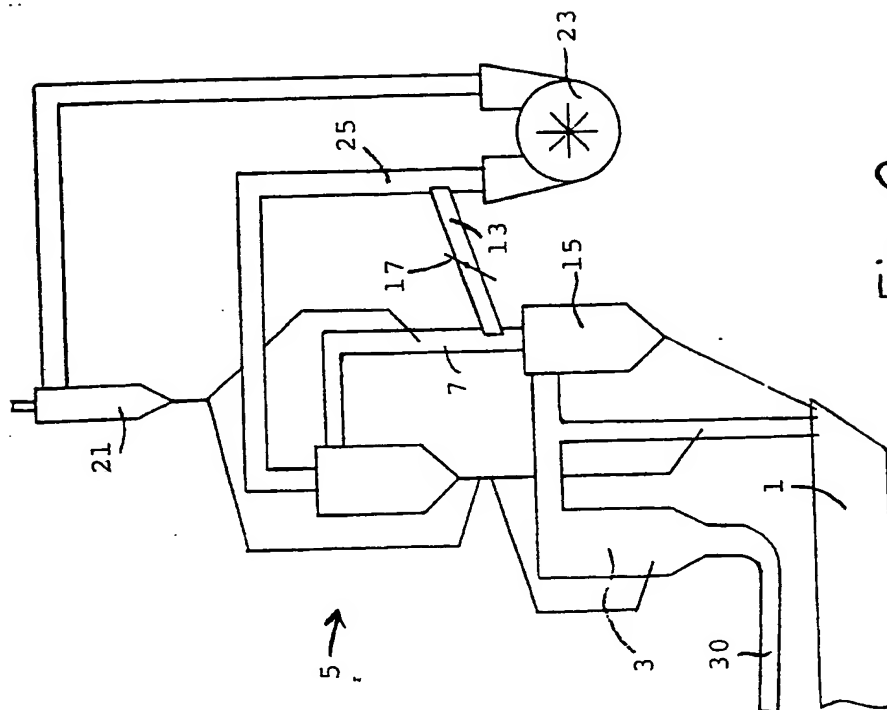


Fig. 2.

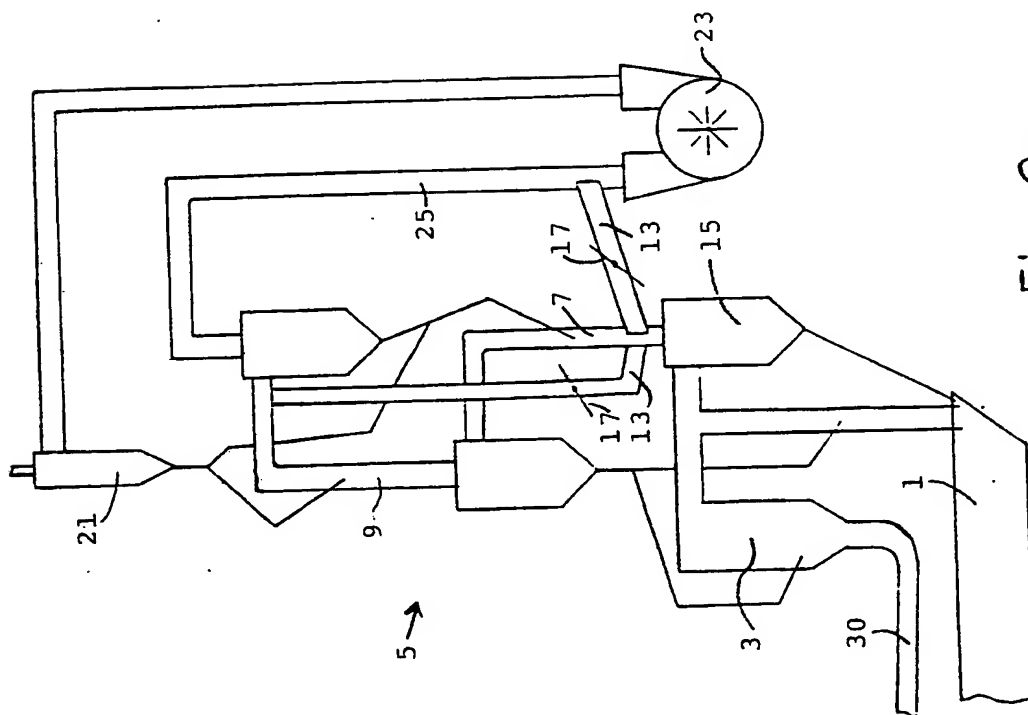


Fig. 3.

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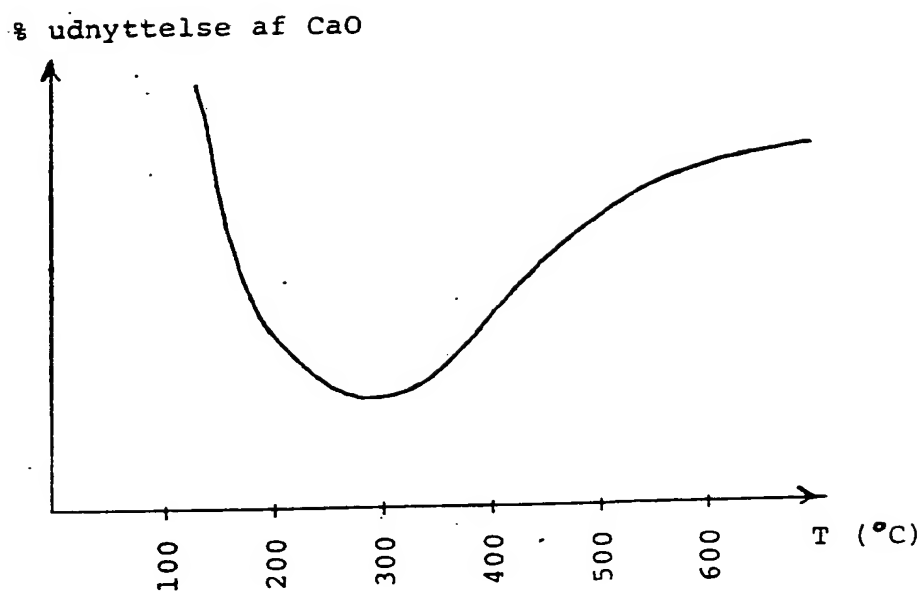


Fig. 5.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/DK 92/00327

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 B01D53/34; C04B7/43; F27B7/20		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	B01D ; C04B ; B01J ; F27B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	AT,B,390 249 (PERLMOOSER ZEMENTWERKE AG) 10 April 1990 see the whole document	1-3,6, 9-11,13, 14,16
Y	---	5,15 7,8
A	PATENT ABSTRACTS OF JAPAN vol. 7, no. 56 (C-155)8 March 1983 & JP,A,57 204 225 (MITSUBISHI JUKOGYO K.K.) 14 December 1982 see abstract; figures 1,3-5	5,15
A	---	1-3,10, 11
A	EP,A,0 111 033 (VEREIN DEUTSCHER ZEMENTWERKE E.V.) 20 June 1984 see the whole document	1-3,5, 8-11,13, 15,16
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search 17 MARCH 1993		Date of Mailing of this International Search Report 07.04.93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer STEVNSBORG N.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category ^o	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	FR,A,2 543 132 (KLÖCKNER-HUMBOLDT-DEUTZ AG) 28 September 1984 see abstract see page 2, line 10 - page 4, line 15 see page 7, line 7 - page 8, line 12 see figure 1 ---	1-3,5,6, 8-11, 13-16
A	DE,A,3 905 453 (KRUPP POLYSIUS AG) 23 August 1990 see column 1, line 65 - column 2, line 22 see column 3, line 54 - column 4, line 67 see figure 1 ---	1-3,10, 11,13,14
A	IEEE TRANSACTIONS ON INDUSTRY APPLICATIONS vol. 25, no. 3, May 1989, NEW YORK US pages 486 - 494 BORGHOLM, H.E. & NIELSEN, P.B. 'Aalborg Portland Converts to the Semi-Dry Process' see the whole document -----	4,12

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

DK 9200327
SA 67701

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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17/03/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
AT-B-390249	10-04-90	None	
EP-A-0111033	20-06-84	None	
FR-A-2543132	28-09-84	DE-A- 3310129	27-09-84
		GB-A- 2139332	07-11-84
		JP-A- 59227749	21-12-84
DE-A-3905453	23-08-90	None	